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Updated Determination of Sulfur and Other Trace Element Content of Fuel Oil in New York State

Final Report

July 2017

17-11

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Updated Determination of Sulfur and Other Trace Element Content of Fuel Oil in New York State

Final Report

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Abstract

This report presents the results of a sampling analysis of No. 2 heating oil and No. 6 residual fuel oil samples collected at fuel oil distribution terminals across New York State from October 2015 to September 2016. It provides an update and point of comparison to a fuel oil sampling analysis previously reported in a 2010 NYSERDA study that covered sulfur content and the trace elements mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb). This more recent analysis also now includes analysis for nitrogen in the fuels. Since the 2010 study, there have been at least three major changes in NYS fuel markets warranting a new look at fuel oil trace element content. First, the State now has requirements to limit the allowable sulfur content in heating and residual fuel oils that were not in effect prior to the 2010 study. In addition, New York City adopted a local rule that phased out the use of No. 6 residual oil in buildings by 2016 and lowered the allowable sulfur content in No. 4 fuel oil (a blend of No. 2 and No. 6) used as a replacement for No. 6. This more recent fuel oil analysis is first, an opportunity to investigate if the changes in sulfur content also affected other trace element concentrations, including metals. Second, there was a temporary shift in the source regions for crude oil used in East Coast refineries, with an increase in crude oil sent by rail from the North Dakota Bakken shale fields starting around 2013 and dropping off again during 2016. The Bakken shale source of crude did not exist in a significant amount prior to the 2010 study. This situation provided an opportunity for a real-world experiment to test if the shift in crude oil source regions at that time had a significant impact on the trace element content of refined fuel oils combusted in NYS. Third, the United States Environmental Protection Agency's (EPA) 2011 National Air Toxics Assessment (NATA), using the 2011 National Emissions Inventory (NEI) data has been released, and it underpredicts the ambient air, nickel concentrations in the NYC metropolitan area from point and nonpoint sources. The 2010 NYSERDA study results, however, indicated lower nickel content in No. 2 heating oil, but higher nickel content in No. 6 residual oil than would be estimated using standard EPA emission factors used in the NEI. This more recent fuel oil assessment provides an opportunity to compare nickel and other trace element concentrations in ambient air to what would be estimated from their measured content in fuel oils combusted in NYC and to the NATA study.

Keywords

Heating oil, distillate oil, residual oil, biodiesel, ultra-low sulfur diesel, mercury, nickel, vanadium, sulfur, trace elements, metals, emission inventory

Acknowledgments

NESCAUM thanks the fuel oil distributors Global Partners, Buckeye Partners, and Sprague Energy for providing access and fuel oil samples for the elemental analysis. We also thank previous NESCAUM staff Leiran Biton, now with the United States Environmental Protection Agency, and Andrew Dick, now with the Oregon Department of Transportation, for their contributions to the study while at NESCAUM.

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Acronyms and Abbreviations

AP-42	air pollutant emissions factors compiled by EPA
B100	biodiesel (pure)
EIA	Energy Information Administration
gal	gallon
ICP-MS	inductively coupled plasma mass spectrometry
kg	kilogram
lb	pound
MDL	method detection limit
mg	milligram
NATA	National Air Toxics Assessment
NEI	National Emissions Inventory
NESCAUM	Northeast States for Coordinated Air Use Management
No. 2 oil	lighter fuel oil cut used for heating oil and highway diesel; also called distillate
No. 4 oil	blend of No. 2 and No. 6 fuel oils
No. 6 oil	high-viscosity residual oil
NYS	New York State
DEC	New York State Department of Environmental Conservation
NYSERDA	New York State Energy Research and Development Authority
PADD	Petroleum Administration for Defense District
ppb	parts per billion
ppm	parts per million
QA/QC	quality assurance and quality control
SEDS	State Energy Data System
ULS	ultra-low sulfur
ULSD	ultra-low sulfur diesel
EPA	United States Environmental Protection Agency

Executive Summary

In 2010, the Northeast States for Coordinated Air Use Management (NESCAUM) completed an analysis for the New York State Energy Research and Development Authority (NYSERDA) to determine levels of sulfur and 10 trace elements (mainly metals) in distillate and residual oil samples collected from terminals in New York City, Albany, and eastern Massachusetts. In short, the 2010 study found the trace element content in fuel oils to be comparable to or less than would be inferred from standard United States Environmental Protection Agency (EPA) emission factors, except for nickel and antimony. An important example of a much lower result was mercury, which the 2010 study found to be at concentrations an order of magnitude lower than would be estimated from EPA emission factors. On the other end of the spectrum, the average nickel concentration found in No. 6 residual oil samples was about 60% higher than would be expected based on the EPA emission factor.

Since the 2010 study, three major events have occurred that warrant revisiting fuel trace element content in New York State. First, the New York State Department of Environmental Conservation (DEC) amended a rule that took effect in 2013 to lower the allowable sulfur content in No. 2 heating oil and No. 6 residual oil statewide, and this was later followed by the adoption of lower sulfur regulations in most other northeast and mid-Atlantic states. In addition, New York City phased out the use of No. 6 residual oil in buildings by 2016 and lowered the allowable sulfur content in No. 4 fuel oil (a blend of No. 2 and No. 6 fuel oils) where it replaced No. 6 residual oil. It is unknown if lowering the sulfur content in fuel oil also affects other trace element levels, including metals.

Second, there was an unforeseen and unprecedented expansion beginning around 2013 in the amount of crude oil passing through NYS by rail from the North Dakota Bakken shale oil fields on the way to East Coast refiners, which dropped off by the end of 2016. This provided an opportunity for a real-world experiment to test if the shift in source regions for crude oil at that time had a significant impact on the trace element content of refined fuel oils combusted in NYS.

Third, air quality modeling by EPA for the 2011 National Air Toxics Assessment (NATA) using 2011 National Emissions Inventory (NEI) data underpredicts nickel concentrations in ambient air in the NYC metropolitan area from point and nonpoint sources. For No. 6 residual oil combustion, the EPA emission factor for nickel is lower than what would be inferred from the fuel oil nickel results in the 2010 NYSERDA study.

To investigate possible changes in fuel trace element content in NYS due to changes in fuel properties and source regions, NESCAUM has analyzed No. 2 heating oil and No. 6 residual fuel oil samples collected at fuel oil distribution terminals across NYS from October 2015 to September 2016. These results are compared to a fuel oil sampling analysis previously reported in the 2010 NYSERDA study. The fuel oil analysis covers sulfur and nitrogen content and the trace elements mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb).

For No. 2 heating oil, mercury content in all the analyzed oil samples was below the method detection limit (MDL) of 10 ppb (parts per billion) used in this study, and is consistent with the low mercury levels measured in the 2010 NYSERDA results. Both studies consistently found lower mercury levels in No. 2 heating oil than would be estimated using the standard EPA mercury emission factor for this fuel.

Where emission factors are reported in the 2010 NYSERDA study for other trace elements (As, Se, Ni, Zn) in No. 2 heating oil, fuel oil analysis from this more recent analysis indicates higher concentrations. Of particular note, nickel levels in No. 2 heating oil were higher than the 2010 NYSERDA results by more than an order of magnitude.

For No. 6 residual oil, all trace elements except antimony, manganese, and nickel were detected at higher levels in this study compared to the 2010 NYSERDA results. The mercury levels measured in the samples were an order of magnitude higher than the 2010 results, although in this more recent study only 10 of the 21 samples of No. 6 residual oil had mercury levels above the MDL.

In comparison to standard EPA emission factors for No. 6 residual oil, all trace elements measured in this study suggested higher emission rates, with some higher by more than an order of magnitude (As, Hg, Se, Pb, Zn). Although this study measured potentially higher trace element levels, we note that No. 6 residual oil was largely phased out of use in New York City when this sampling effort was underway in 2016.

1 Introduction

In 2010, NESCAUM completed an analysis for NYSERDA to determine levels of sulfur and 10 trace elements in distillate and residual oil samples collected from terminals in New York City, Albany, and eastern Massachusetts (NYSERDA 2010). The 10 trace elements, or their compounds, can have toxic impacts on human health, depending on an individual's dose and extent of exposure. The known toxic effects for each element have been compiled by the United States Department of Health and Human Services Agency for Toxic Substances & Disease Registry (ATSDR 2014).

Fuel oils were the focus of the 2010 study due to their perceived, relatively large contribution to mercury air emission inventories in New York State and other northeastern states. Studies of crude oil in North American markets, however, suggested that actual mercury emissions from fuel oil combustion could be substantially lower than estimates based on standard EPA emission factors (AP-42 factors). The study, which analyzed fuel samples taken during 2008 and 2009 from major oil distributors in the region, corroborated this hypothesis. Mercury concentrations in oil were an order of magnitude lower than estimates based on AP-42 factors.

More generally, the 2010 study found the trace element content in fuel oils to be comparable to or less than EPA AP-42 emission factors except for nickel and antimony. For example, the average nickel concentration of the analyzed residual oil samples was about 60% higher than would be expected based on the AP-42 emission factor. This raised an important health concern, as research suggests an association between nickel (and vanadium) concentrations in fine particulate matter and average daily mortality risk (Lippmann et al. 2006). Air quality monitoring and exposure studies conducted in New York City observed higher nickel and vanadium concentrations in the City – especially in Bronx and New York Counties – than in surrounding areas (Patel et al. 2009; Peltier et al. 2009; Peltier & Lippman 2010). The primary source of these trace metals is believed to be residual oil combustion boilers, which is consistent with higher nickel concentrations observed in winter than in summer.

Since the 2010 study, three major changes have occurred in NYS that warrant a second round of fuel oil analysis for trace elements. First, the DEC amended a rule that took effect in 2013 to lower the allowable sulfur content in No. 2 heating oil and No. 6 residual oil, and this was later followed by the adoption of lower sulfur regulations in most other northeast and mid-Atlantic states. The DEC requirement limited No. 2 heating oil sulfur content to 15 parts per million (ppm). For comparison, the No. 2 heating oil samples analyzed in the 2010 study averaged almost 2,000 ppm sulfur content. For No. 6 residual oil, the 2013 NYS rule amendment limited sulfur content to 3,000 ppm in New York City, 3,700 ppm in Nassau and Westchester Counties, and 5,000 ppm in the rest of the State. Note that in the 2010 study, No. 6 sulfur content averaged 3,020 ppm, similar to the limit for downstate counties in the 2013 rule. We also note that New York City adopted a rule in 2011 that resulted in largely phasing out No. 6 fuel oil at boilers in the City by 2016, and limited sulfur content in No. 4 fuel oil (a blend of No. 2 and No. 6 fuel oils) to 1,500 ppm, with a phaseout in use of No. 4 fuel oil completely by 2030. The combination of NYS and New York City sulfur requirements are expected to have significant public health benefits resulting from the reduction in human exposure to fine particulate matter and the nickel it contains (Kheirbek et al. 2014).

Second, there was a temporary but large shift in the source regions for crude oil shipped to East Coast refineries, with an increase in crude oil from the North Dakota Bakken shale fields starting around 2013 and dropping off again during 2016. This oil typically went through NYS by rail to the Port of Albany, where it was transferred to barges for shipment to refineries on the East Coast. An oil industry analyst predicted that in 2014 about 800,000 barrels per day of Bakken oil shale crude would be shipped to East Coast refineries (Philips 2013), which would be equivalent to about 60% of the region's total refinery capacity. This source of crude did not exist in a significant amount prior to the 2010 study, and created the opportunity for a real-world experiment to examine if the shift in crude oil source regions during this period significantly affected the trace element content of fuel oils combusted in NYS.

Third, air quality modeling by EPA for the 2011 NATA using 2011 NEI data underpredicts the nickel concentrations in ambient air in the NYC metropolitan area from point and nonpoint sources. One reason is that there are no emission factors for some source classification codes from which the point/nonpoint inventories are derived. Where emission factors are available, they are lower than what would be inferred from the fuel oil nickel results in the 2010 NYSERDA study.

Given these developments, this study updates the 2010 report by obtaining and analyzing new No. 2 and No. 6 fuel oil samples in a “Phase 2” sampling program to determine whether trace element composition has changed in fuel oils sold in NYS. This report updates the fuel oil sampling analysis in NYS for sulfur content and the trace elements mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb). It is timely and appropriate to reassess the chemical composition of fuels used in NYS in light of the widespread changes in sulfur content of the fuels, the profound shift in the source for crude oil used in East Coast refineries, and the clear differences between modeling results versus actual measurements of key elements in NYS fuels, particularly nickel.

2 Fuel Oil Market Assessment and Literature Review

This section provides an update of an earlier fuel market assessment and literature review from 2010 (NYSERDA 2010) using information over the five-year period from 2010 to 2015. This gives an overview of the fuel market overlapping the sampling period from October 2015 to September 2016; however, as indicated in this section, source regions supplying East Coast refiners with crude oil have since changed. Therefore, this assessment reflects a "picture in time" of the fuel oil market during the sampling period that has now shifted.

The goals of the market assessment were as follows:

- Identify the sources of crude oil used to make refined oil products for the NYS marketplace during the sampling period, with the additional goal of determining what share Bakken shale oil may have had in the NYS fuel oil market.
- Track changes in market conditions since 2010, specifically recent rules requiring lower sulfur content in heating oil.
- Aid in designing a sampling plan that is geographically representative of fuel oils distributed in NYS.

We also sought to update the literature review in the 2010 study by searching for more recent published information on trace element content of fuel types that may have appeared since that report.

2.1 Statewide overview

According to the Energy Information Administration (EIA) State Energy Data System (SEDS), about one-quarter of households in NYS used heating oil (EIA 2016a) compared to a national average of only 5.1% in 2015 (U.S. Census Bureau, 2016). The EIA (2016b) also reports that NYS was the highest consuming state for residential distillate fuel in the United States in 2015, representing 22% of domestic consumption. Other states in the Northeast consume the next highest shares, with Pennsylvania (16%), Massachusetts (15%), and Connecticut (11%), comprising the next three highest residential distillate oil-consuming states for 2015.

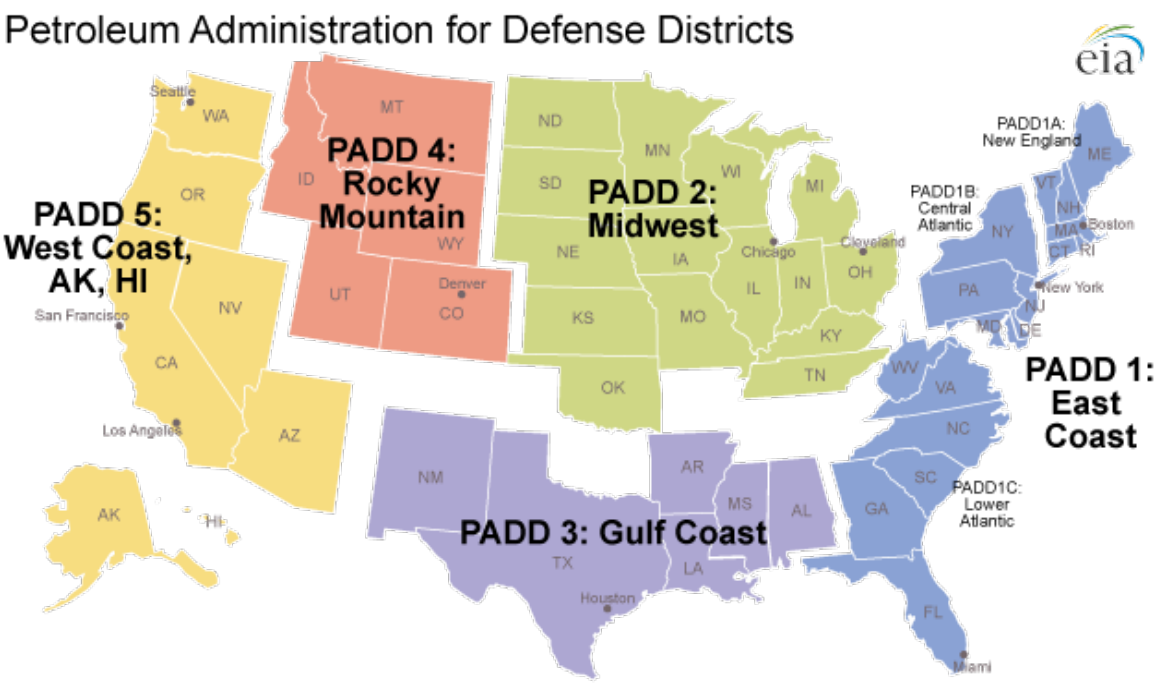
2.1.1 Crude oil sources to New York State and the role of the Bakken Shale

This section describes NESCAUM's efforts using available information to identify crude oil feedstocks entering NYS and the Northeast region during the sampling period. A set of analytic tools developed by NESCAUM are used to track crude oil feedstocks and upstream carbon emissions associated with petroleum fuels consumed in the Northeast. Key inputs to these tools include imports of crude oil or liquid fuels to different areas of the country or exchanges between different regions. These regions are known as Petroleum Administration for Defense Districts (PADDs) and were delineated during World War II to manage liquid fuels allocation. They remain the reporting standard for many datasets. Figure 1 is a map of these PADDs.

NESCAUM applied its in-house Carbon Intensity (CI) Tracking Tool, developed in 2013, that incorporates data from a number of sources to estimate the share of regional petroleum fuel sources from different crude oil source regions. Initially, NESCAUM relied on high-level summary data for imports of crude oil and finished product to each PADD, other fuel movements (EIA 2011), and some foreign data, such as crude oil exports reported by Canada's National Energy Board (2011). Later, NESCAUM's analysis incorporated the proprietary Port Import/Export Reporting System database (IHS 2011), which provides additional information on crude oil imports to the refining regions serving the East Coast's PADD 1.

Figure 1. Map of Petroleum Administration for Defense Districts (PADDs)

Source: Reproduced from EIA 2011



The EIA data (2011) illustrate several pathways by which gasoline and distillate fuel have been supplied to PADD 1. Circa 2011, about 21% of the volume was imported to PADD 1 as foreign crude oil, and then refined at 10 refineries in the East Coast states. Roughly 58% of the volume was refined along the Gulf Coast (i.e., in PADD 3) from a mix of domestic and imported crude oil and then shipped to PADD 1 as a refined product. Products imported to PADD 1 from foreign sources as refined fuels accounted for 20% of the total volume. About 1% of the volume was refined in PADD 2 (the Midwest) and supplied to PADD 1 as a finished product.

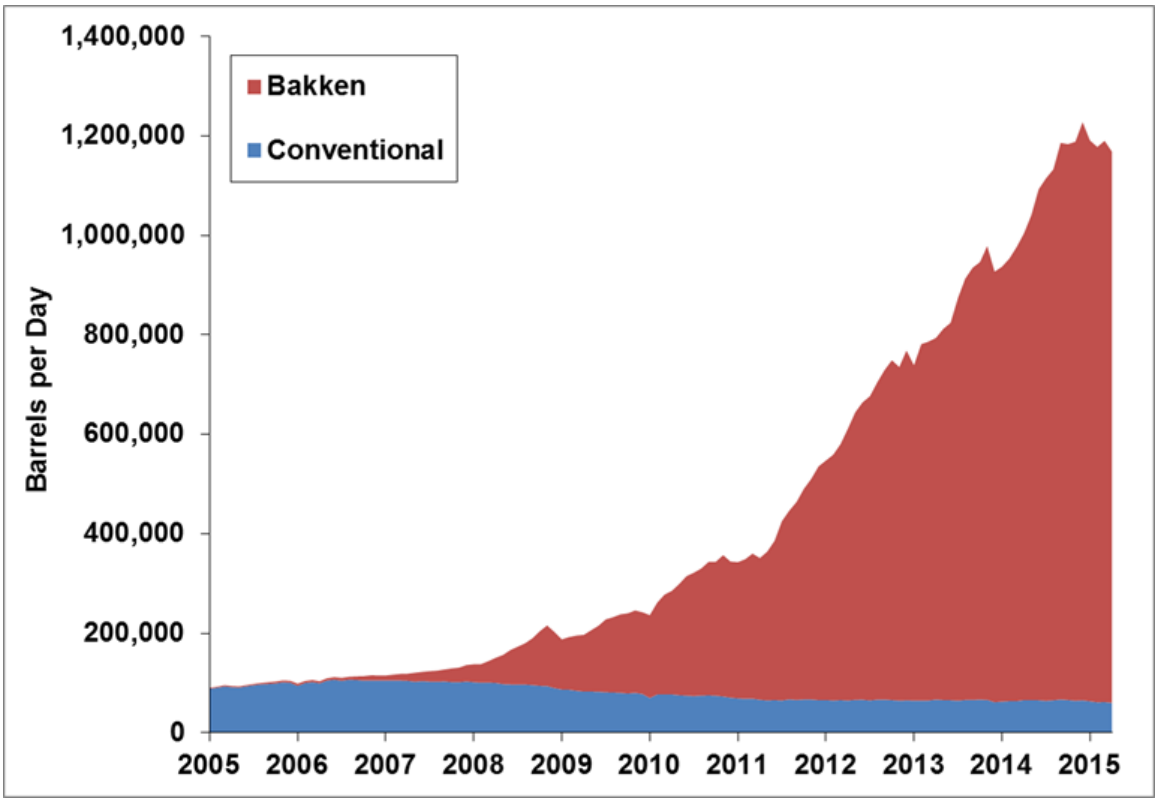
The East Coast produces very small volumes of crude oil domestically, accounting for less than 2% of crude oil inputs to the region. The overwhelming majority of crude oil inputs to PADD 1 at the time of the 2010 study were imported from abroad. The inputs reflected a very diverse mix of supplying countries, with significant quantities from the Eastern Seaboard of Canada, Central and South America, West Africa, the Middle East, and the North Sea. As of 2011, East Coast refineries had not yet begun receiving rail shipments of Bakken crude, and were receiving very limited quantities of synthetic and blended bitumen crudes from the Alberta tar sands, which accounted for less than 6% of Canadian imports to PADD 1 and less than 0.3% of total crude oil feedstock for fuels consumed in the region.

Following the rapid increase in crude oil production from the Bakken formation in North Dakota, many East Coast refineries began to substitute crude oil imported from foreign sources with light, low-sulfur crude oil from the Bakken development. Figure 2 shows the rapid expansion in production from the Bakken formation since 2005 relative to conventional crude sources in North Dakota.

By the end of 2013, Bakken crude was supplying at least 400,000 barrels per day by rail to East Coast refineries. Information from EIA suggested that crude transported by rail—the majority of it from the Bakken—accounted for as much as 52% of crude oil processed in East Coast refineries, or about 452,000 barrels per day by early 2015 (EIA 2015b). For perspective, the total operating refinery production capacity in PADD 1 was roughly 1.3 million barrels per day (EIA 2015a).

Figure 2. North Dakota oil production, January 2005 through April 2015

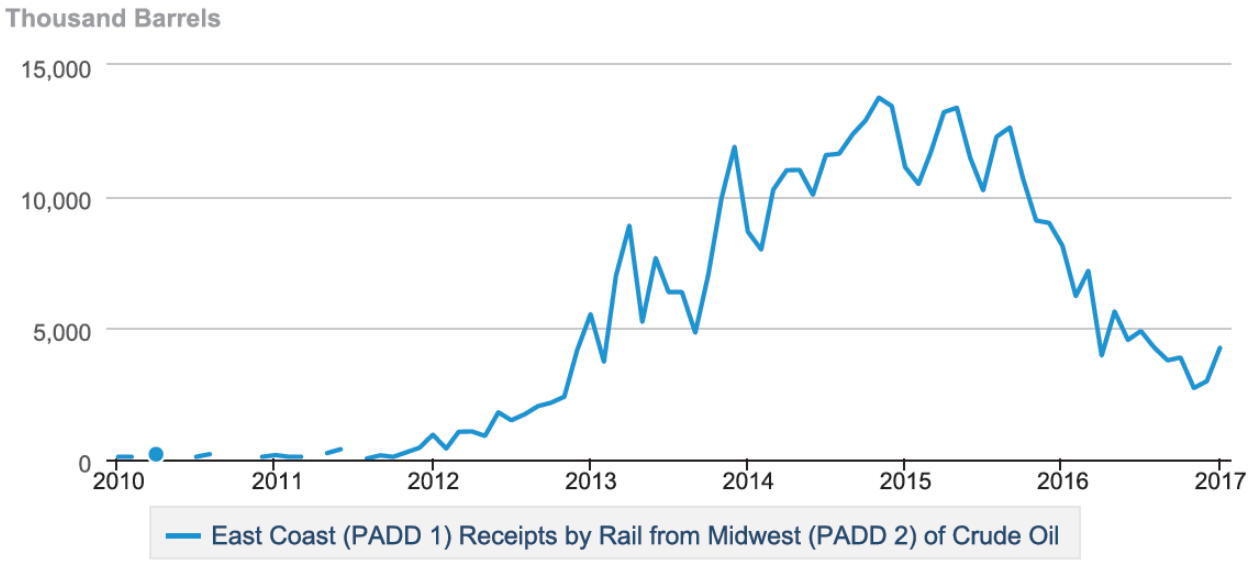
Source: North Dakota Department of Mineral Resources (2015)



We note that during the time of the sample collection for this study, rail shipments from the Midwest (PADD 2) to the East Coast (PADD 1) were in decline after their rise beginning in 2013 (Figure 3). This was due in part to the changing economics of crude-by-rail transport, which reflect the price differences between domestic and international crude oils (EIA 2016c). As crude prices narrowed between Midwest oil and crude imported from the North Sea, East Coast refiners were more likely to process imported crudes than rail-transported domestic supplies. In addition, the opening of new pipelines and declining domestic production in the Midwest and Gulf Coast, onshore regions may have also contributed to the declining rail shipments to PADD 1. With these changes, crude supply regions have shifted since the period of this study's sampling collection, and the results presented here are a snapshot in time of market conditions.

Figure 3. East Coast (PADD 1) receipts by rail from Midwest (PADD 2) of crude oil

Source: U.S. Energy Information Administration, Movements of Crude Oil and Selected Products by Rail (release date March 31, 2017)



Under the conditions during the study period, if all crude oil inputs to PADD 1 were distributed equally as feedstocks for fuels consumed in different parts of the region, the quantities of Bakken crude by rail would account for 11% of the crude feedstock for all petroleum fuels consumed in PADD 1. However, PADD 1 stretches from Maine to Florida, so crude sources distributed, refined, and used in different parts of the region may vary significantly due to the configuration of the petroleum distribution infrastructure.

In addition to rail transport of crude oil, pipelines bring in refined products to the PADD 1 area as well. The Colonial Pipeline has an overall capacity of 100 million barrels per day, and travels through the Southeast, bringing refined products from Gulf Coast refineries to terminals in Mississippi, Alabama, Georgia, and up the Atlantic Coast before terminating at the Port of New York and New Jersey. Petroleum products refined in the Gulf Coast and offloaded from the Colonial Pipeline may be disproportionately consumed in the southeastern states. However, East Coast refineries in New Jersey and Pennsylvania (the same refineries that received increased shipments of Bakken crude) account for a greater share of the fuel consumed in NYS than they do for the entire PADD 1 region. This is supported by a New York City report (2013) that provides estimates for volumes of petroleum products entering the New York City region from different pathways. The report estimated that 41% of New York City's supply was provided by regional refineries, 36% by pipeline, and 23% by marine tanker. Compared to the shares for PADD 1 as a whole, the New York City region receives a greater share from the regional refineries. With Bakken accounting for up to 52% of crude oil inputs to East Coast refineries around the time of this study, up to 21% of petroleum fuels consumed in the New York City region may have been derived from Bakken crude. As described in the next section, different geographic subregions of NYS were probably supplied with mixes of fuels sourced from different supply regions.

2.1.2 Oil types and distribution

According to a NYSERDA review of fuel terminals (ICF 2014), about 25% of NYS terminals account for about 65% of the refined petroleum product throughput at all NYS terminals. These terminals each supply on average at least 15,000 barrels per day. The highest throughput levels for refined products at NYS terminals were in Long Island, the Capital District (Greater Albany), and New York City. Heating oil represented about 23% of the throughput at NYS terminals, and diesel accounted for about 14%. These fuels were available at 93% of surveyed terminals. No. 6 residual fuel oil accounted for about 5% of the throughput at these terminals (ICF 2014). Since the ICF (2014) review, No. 6 residual oil for commercial buildings has been phased out of use in New York City, therefore current throughput of No. 6 residual oil at terminals in NYS may have since declined or ended.

Since the ultra-low sulfur (ULS) heating oil requirements came into effect in NYS, many terminals have consolidated their storage of ultra-low sulfur diesel (ULSD) and ULS heating oil, which are essentially the same product with different dyes. Figure 4 shows the implementation dates for the ULSD requirements in the northeastern states.

Figure 4. Timeline of northeastern states' rules for sulfur content in heating oil

Source: Reproduced from EIA 2012

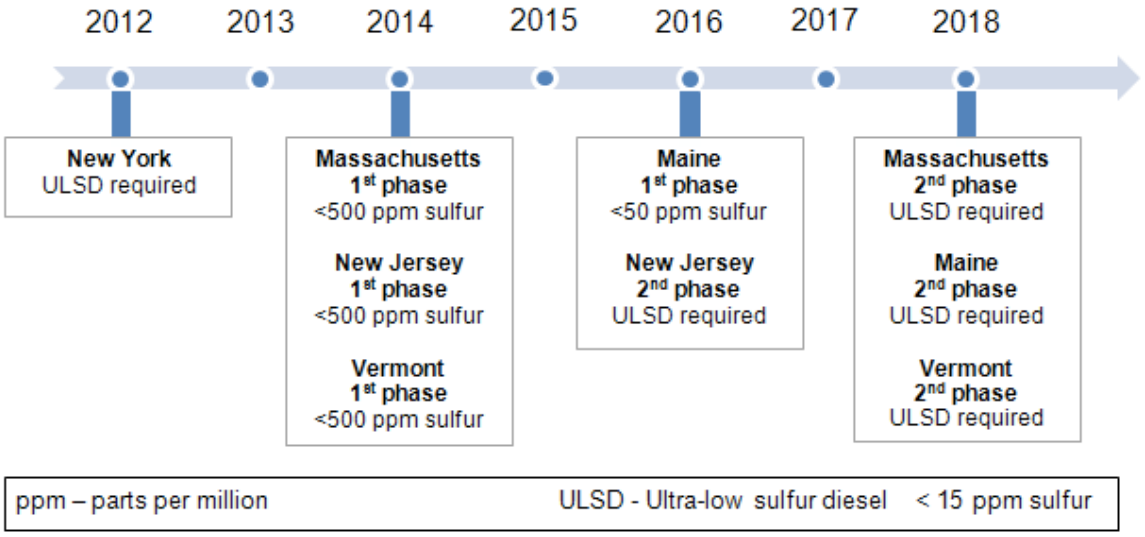


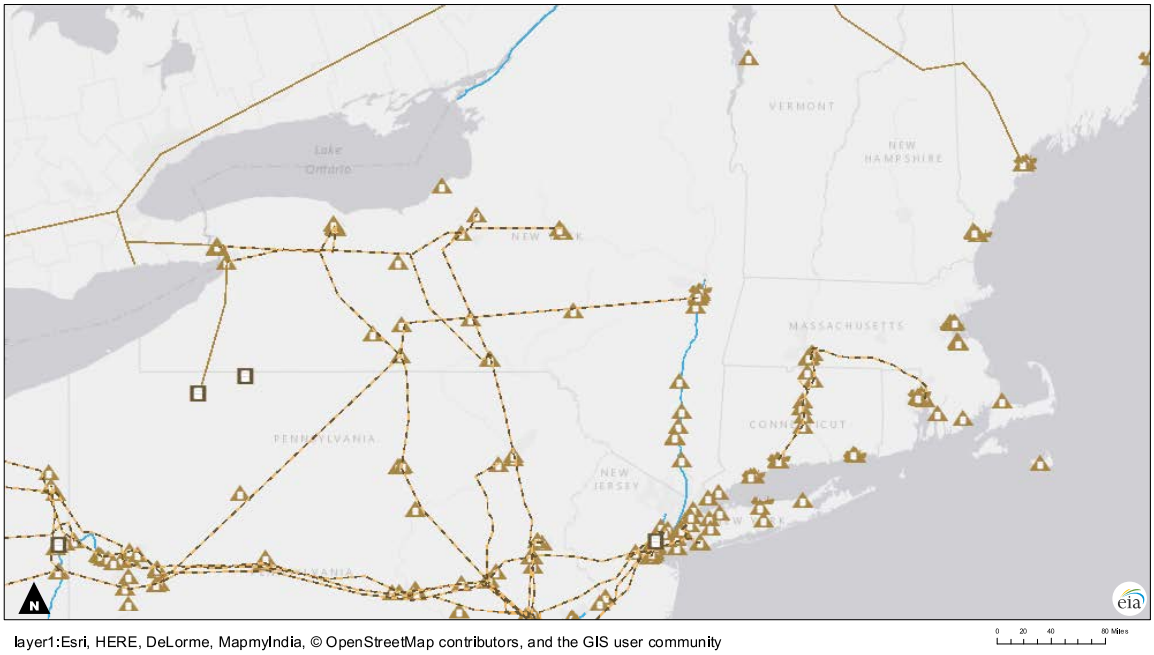
Figure 5 summarizes the major transportation infrastructure for crude oil and refined petroleum products in NYS. ICF (2012) provides details on the distribution of refined oil products into NYS and is summarized here for items pertinent to the current study:

- The Colonial Pipeline extends through Pennsylvania to the New York City area, where it spurs into the Buckeye system. Colonial transports refined product from the Gulf Coast (i.e., Texas and Louisiana).
- Buckeye Partners operates pipelines with product collected from the Colonial Pipeline, refineries, and marine terminals to serve the NYS area. Buckeye Pipelines supply New York City and Long Island, as well as transport fuel across Pennsylvania through the Binghamton area, extending northward to Syracuse and westward to Rochester and Buffalo/Tonawanda.
- The Sunoco Logistics Pipeline transports fuels from Pennsylvania refineries into western New York, including Rochester and Tonawanda.

Figure 5. Map of major petroleum infrastructure in New York State

Refined petroleum product pipelines marked as dashed yellow/brown lines; crude oil pipelines marked as brown lines; marine petroleum shipping routes marked as blue lines; petroleum terminals marked as brown triangles; petroleum refineries marked as brown squares.

Source: Energy Information Administration (EIA) map: http://www.eia.gov/state/maps.cfm



Refined petroleum products (e.g., ULSD, No. 2 oil, No. 6 oil) are shipped via marine transport, rail, and pipeline into NYS from both domestic and foreign source regions. The Buckeye system in particular is a key component in the distribution of these refined products across NYS. The Buckeye terminal in Linden, New Jersey serves as a distribution hub that consolidates supplies from pipeline and marine infrastructure and transports them westward to cities in Upstate New York and eastward to Long Island (ICF 2012).

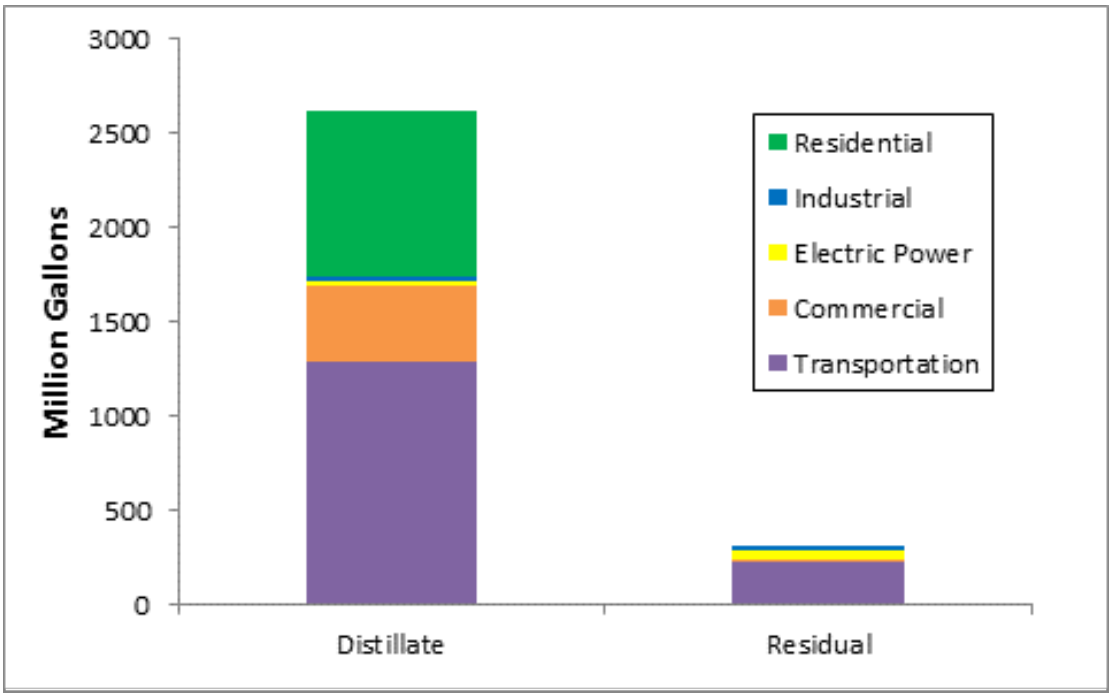
Points from New York Harbor and the Hudson River up through the Capital District are also supplied by a mix of foreign imports and domestic marine shipments.

2.1.3 Representing the fuel mix

According to EIA (2016d), about 308 million gallons of residual fuel oil and 2.6 billion gallons of distillate fuel were consumed in NYS in 2015 across all sectors. These data are presented by sector in Figure 6. The dominant uses of No. 2 distillate oil in NYS in 2015 were for commercial and residential heating as well as for transportation (i.e., diesel fuel). The largest use in NYS in 2015 of No. 6 residual oil was transportation (i.e., vessel bunkering fuel oil), followed by electricity generation.

Figure 6. 2015 No. 2 distillate and No. 6 residual fuel oil consumption by sector in New York State (million gallons)

Source: EIA 2016d

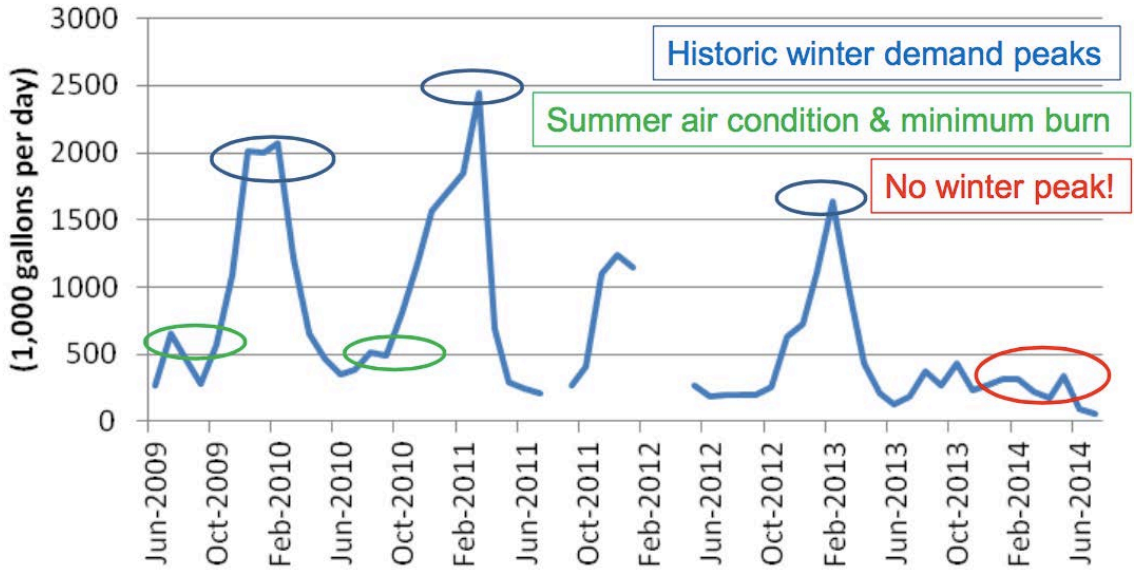


According to the NYSERDA Patterns and Trends report (2014), residual fuel oil consumption has greatly decreased—by about 67%—in NYS in the last decade, while distillate fuel oil use has fallen by about 20% over that time.

As shown in Figure 6, uses for No. 6 residual fuel oil in NYS are primarily in the transportation and electric power sectors. Commercial use of No. 6 oil in New York City apartment building boilers has declined significantly since 2011, as New York City's Clean Heat Program has resulted in the phase out of residual fuel in commercial buildings (Figure 7). As the Clean Heat Program eliminated residual oil used by building boilers, transportation (specifically, bunker fuel for use in marine vessels) has become the dominant sector for residual fuel oil consumption in NYS.

Figure 7. New York State No. 6 residual fuel oil sales/deliveries, 2009–2014

Source: Reproduced from NYSERDA (2014b)



2.2 Literature review

NESCAUM conducted a literature review to search for information on trace element content analyses of refined petroleum fuels appearing since the publication of the 2010 NYSERDA report. Since the 2010 report, it appears that no peer-reviewed scientific articles have been published that focused on fuel oil surveys with trace element analyses.

NESCAUM searched for published literature that directly cited either the NESCAUM report or the Wilhelm et al. report (2007) titled *Mercury in Crude Oil Processed in the United States (2004)* referenced in the 2010 NYSERDA report. Neither search found any new literature that would inform this current effort. The researchers also broadened the search to include any article focusing on trace elements in refined oil products. NESCAUM included crude oil as well as refined oil products in the search terms. Finally, the researchers focused solely on Bakken shale rather than on global sources of oil. These searches did not find any published articles with information relevant to this work.

Based on this review of available literature, the current effort will provide a valuable dataset not currently available in the public domain for trace elements and their potential correlation with sulfur in refined fuel oil.

3 Fuel Oil Analysis

In this section, we present the fuel oil elemental analysis results and compare them with the earlier fuel oil analysis from 2010 (NYSERDA 2010). The fuel oil sampling began in October 2015, with sample collection and analysis continuing until September 2016. Four fuel oil types were included in the testing: No. 2 heating oil, No. 6 residual oil, ultra-low sulfur diesel, and biodiesel. The majority of fuel samples were for No. 2 heating oil. In total, 162 samples and 6 duplicates from 15 fuel storage tanks across the State were collected and tested for trace elements, sulfur, and nitrogen.

3.1 Terminal identification and outreach

In order to identify candidate fuel oil terminals for the Phase 2 fuel oil sampling, NESCAUM compiled a list of 72 terminal locations across the State extracted from company websites and a list maintained by the United States Internal Revenue Service (IRS 2015). Figure 8 displays a map of these locations.

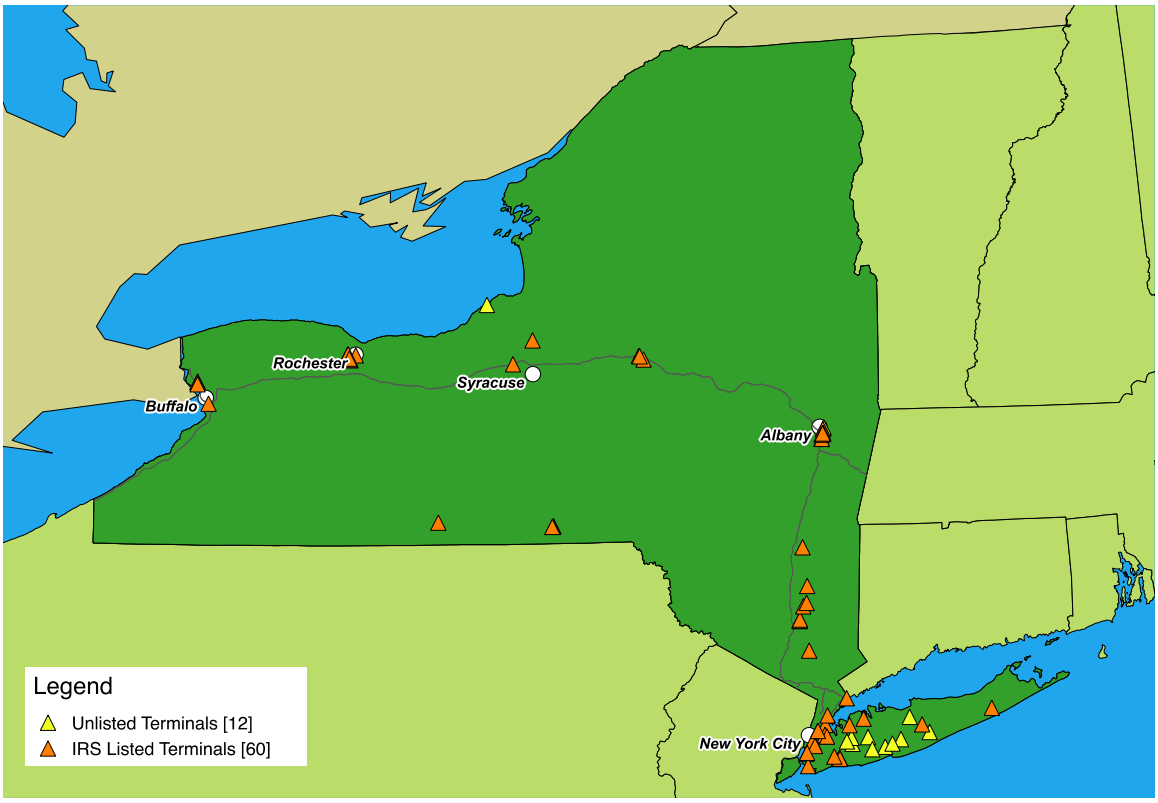
Examination of the distribution of oil terminals indicated key regions to be assessed in the fuel oil sampling and analysis. These regions are defined as:

1. Buffalo/Tonawanda
2. Rochester
3. Greater Syracuse region
4. Utica
5. Capital District
6. New York City
7. Long Island
8. Hudson Valley
9. Southern Tier along the Pennsylvania border

Figure 8. Map of fuel oil terminal locations in New York State

Terminals marked in orange are listed by the IRS; terminals marked in yellow are listed on industry websites, and not by the IRS.

Sources: IRS 2015; industry websites.



Buckeye Partners (serving all markets except Long Island) and Global Partners (serving six of eight markets, including Long Island) are the largest distributors in the NYS fuel oil market by coverage area. Sprague Energy serves three markets. However, Irving Oil, which was included in the 2010 study at its Revere, Massachusetts terminal, does not currently appear to have a major presence in NYS. Several other terminal operators were identified, but many of these companies appear to only operate in one or two NYS regions.

Based on the regional terminal locations and their ownership and the desire to include sampling from one or more terminals in western NYS, NESCAUM approached Buckeye Partners as a potential participant in the Phase 2 sampling strategy. NESCAUM also approached Global Partners and Sprague Energy due to their large NYS market presence and past participation in the Phase 1 fuel oil sampling. All three companies agreed to participate in Phase 2.

NESCAUM selected 15 terminal sites operated by the three companies that reflect eight fuel distribution regions in NYS. Table 1 lists the selected terminals and their distribution regions, and Figure 9 is a map of the selected terminal locations.

Table 1. List of fuel terminal locations selected for sampling in New York State

Region	Distributor	Terminal Location
Buffalo/Tonawanda	Buckeye Terminals	Buckeye-Buffalo
Capital District	Global Partners	Global-Albany
	Sprague Energy	Sprague-Albany (Rensselaer, NY)
Greater Syracuse	Buckeye Terminals	Buckeye-Brewerton
Hudson Valley	Global Partners	Global-Original (New Windsor, NY)
	Global Partners	Global-North (New Windsor, NY)
Long Island	Global Partners	Global-Oyster Bay
	Global Partners	Global-Inwood
New York City	Sprague Energy	Sprague-Bronx
	Buckeye Terminals	Buckeye-Bronx
	Buckeye Terminals	Buckeye-Brooklyn
Rochester	Buckeye Terminals	Buckeye-Rochester
	Buckeye Terminals	Buckeye-Rochester South
Southern Tier	Buckeye Terminals	Buckeye-Vestal
Utica	Buckeye Terminals	Buckeye-Utica

Figure 9. Map of fuel oil terminal locations selected for sampling in New York State

A full year of sampling was conducted to capture differences in seasonality. Because No. 2 heating oil is consumed in NYS in much higher quantities compared to No. 6 residual oil, the sampling plan was more weighted towards No. 2 heating oil. Furthermore, because sales and delivery of residual oil in recent years appear to have become relatively constant over the course of a year and no longer appear to be subject to significant seasonal consumption patterns, NESCAUM developed a quarterly sampling for residual oil. For No. 2 heating oil, NESCAUM followed a monthly sampling schedule over the course of a year at 10 terminals, with an additional four terminals sampled during the winter months only (i.e., October through April) to capture potential regional differences during the heating season.

3.2 Testing Methodology

Analysis of fuel oils was performed by a certified and accredited testing laboratory operated by Inspectorate America Corporation (Inspectorate) under contract with NESCAUM. The testing was done over 12 months in a single phase. Testing focused on determining the levels of mercury (Hg), lead (Pb), nickel (Ni), vanadium (V), zinc (Zn), cobalt (Co), arsenic (As), selenium (Se), manganese (Mn), antimony (Sb), sulfur (S), and nitrogen (N) in primarily No. 2 heating oil as well as in a small number of samples of No. 6 residual oil, No. 2 ultra-low sulfur diesel (ULSD), and No. 2 B100 biodiesel.

All samples were analyzed for trace elements by inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS is a type of mass spectrometry that is highly sensitive and capable of detecting and quantifying a range of metals and several non-metals at concentrations in the parts per billion range and below (Ammann 2007). A nebulizer sample droplet is introduced into a charged plasma created at high temperature (~10,000 C) within the instrument. The sample droplet and any solids within it vaporize and break down into atoms. The plasma temperature is sufficiently high enough to ionize an atom into a singly charged ion that has lost its most loosely bound electron. The positively charged ion is then passed through a mass spectrometer (typically a mass quadrupole) where trace element ions can be discriminated according to their mass, with the electronic detection signal proportional to the concentration of the atomic species in the sample droplet.

Nitrogen content of the fuels was tested using an oxidative combustion and chemiluminescence detection method. Sulfur content of the samples was analyzed using ultraviolet fluorescence. Additional details of the sampling approach are given in the following sections.

3.2.1 Analytical Methods

Inspectorate used the following standard laboratory test methods for the fuel oil samples:

1. For trace elements in No. 6 residual oil samples: ASTM D5185 *Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-MS)*. Trace element analysis, including mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se) and lead (Pb).
2. For sulfur in No. 6 residual oil samples: ASTM D4294-10 *Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry*. MDL = 20 ppm, up to 4.6% by mass.
3. For sulfur in No. 2 fuel oil samples: ASTM D5453-12 *Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence*. MDL = l.0 to 8,000 ppm (m).
4. For nitrogen in No. 2 and No. 6 fuel oil samples: ASTM D5762 *Standard Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence* (detection range 40 ppm to 10,000 ppm), and ASTM D4629 *Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection* (detection range 0.3 ppm to 100 ppm).
5. For trace elements in No. 2 fuel oil samples: IAC-027 ICP Mod *Trace metal analysis by inductively coupled plasma*. MDL = 10 parts per billion (ppb).

The minimum detection limits for the trace elements investigated by the ICP-MS technique for No. 2 fuel oil and No. 6 residual oil are shown in Table 2.

Table 2. Elemental method detection limits (MDLs)

Element	No. 2 Fuel Oil	No. 6 Residual Oil (mg/kg)
S	1.0 mg/kg	20
N	0.3 mg/kg	0.3
Hg	10 ppb	0.1
As	10 ppb	0.1
Co	10 ppb	0.1
Mn	10 ppb	0.1
Ni	10 ppb	0.1
Pb	10 ppb	0.1
Sb	10 ppb	0.1
Se	10 ppb	0.1
V	10 ppb	0.1
Zn	10 ppb	0.1

3.2.2 Fuel Oil Sampling

Analyses to determine trace elements, nitrogen, and sulfur content for 162 fuel oil samples were performed as described in this section. Sampling began in October 2015 and continued on a monthly basis until September 2016. No. 2 heating oil represented the majority of samples (131 samples and four duplicates) compared with the limited numbers of residual oil (20 samples and 1 duplicate), ultra-low sulfur diesel (10 samples and 1 duplicate), and biodiesel (B100) (one sample). The 6 duplicate samples (about 4% of total samples) were collected for quality assurance purposes. The sampling plan originally envisioned collecting 32 residual oil samples, but the selected terminals did not always have residual oil in storage at the time of collection. Similarly, the sampling plan originally called for obtaining four B100 biodiesel samples, but lack of product availability at the time of site visits resulted in only one sample collected out of the four originally planned.

Samples were collected at 15 previously identified fuel oil terminals in NYS operated by Sprague Energy, Global Partners, and Buckeye Partners. Additional details on the frequency and location of sampling for the different fuel oil types are shown in Tables 3 and 4. The complete sampling schedule for the entire project period is given in Table 5 (the exact dates samples were collected during each month were at the discretion of the laboratory).

Table 3. Sampling schedule for No. 2 heating oil from October 2015 to September 2016

Terminal No.	Terminal Name	Sampling Schedule	Operator
T-16-NY-1458	Buckeye-Buffalo	Monthly	Buckeye Partners LLC-Buffalo
T-14-NY-1403	Global-Albany	Winter months only	Global Companies LLC
T-14-NY-1417	Sprague-Albany	Monthly	Sprague Operating Resources LLC-Rensselaer
T-16-NY-1456	Buckeye-Brewerton	Monthly	Buckeye Partners LLC-Brewerton
T-14-NY-1413	Global-Original	Monthly	Global Companies LLC
T-16-NY-1499	Global-North	Winter months only	Global Companies LLC
T-11-NY-1336	Global-Oyster Bay	Monthly	Global Commander Terminal
T-11-NY-1305	Global-Inwood	Monthly	Global Companies LLC
T-11-NY-1308	Buckeye-Brooklyn	Winter months only	Buckeye Partners LLC-Brooklyn
T-13-NY-1352	Sprague-Bronx	Monthly	Sprague Operating Resources LLC - Bronx
T-16-NY-1469	Buckeye-Rochester	Monthly	Buckeye Partners LLC-Rochester I
T-16-NY-1488	Buckeye-Rochester South	Winter months only	Buckeye Partners LLC-Rochester II
T-16-NY-1472	Buckeye-Vestal	Monthly	Buckeye Partners LLC-Vestal
T-16-NY-1486	Buckeye-Utica	Monthly	Buckeye Partners LLC-Utica

Table 4. Sampling schedule for No. 6 fuel oil, ULSD, and biodiesel from October 2015 to September 2016

Terminal No.	Terminal Name	Sampling Schedule	Operator
No. 6 Residual Oil			
T-14-NY-1417	Sprague-Albany	Winter months only	Sprague Operating Resources LLC-Rensselaer
T-13-NY-1352	Sprague-Bronx	Monthly	Sprague Operating Resources LLC-Bronx
T-13-NY-1353	Buckeye-Bronx	Winter months only	Buckeye Partners LLC-Bronx
T-11-NY-1308	Buckeye-Brooklyn	Winter months only	Buckeye Partners LLC-Brooklyn
Ultra-low Sulfur Diesel (transportation fuel)			
T-14-NY-1413	Global-Original	Summer months only	Global Companies LLC
T-16-NY-1458	Buckeye-Buffalo	Summer months only	Buckeye Partners LLC-Buffalo
T-16-NY-1488	Buckeye-Rochester South	Summer bimonthly	Buckeye Partners LLC - Rochester II
B100 Biodiesel			
T-14-NY-1417	Sprague-Albany	August only	Sprague Operating Resources LLC-Rensselaer

A smaller subset of monthly samples of No. 2 ULSD (used in transportation) and B100 biodiesel was obtained for four months at three terminals, according to the schedule shown in Table 5. As noted earlier, we were only able to collect one B100 sample during this period due to lack of product availability. ULSD samples were collected in a similar manner as No. 2 heating oil samples, as the fuel oil is essentially the same product at the truck rack except for the dye. Based on the sampling schedule of Table 5 the laboratory collected and analyzed a total of 162 primary samples and six duplicate quality assurance samples over the course of a 12-month period.

All sampling took place at the truck rack, with no samples collected directly from within storage tanks. Sample treatment and analysis followed the previously described laboratory standard test methods. The laboratory followed its standard chain of custody procedure for each sample, as tracked by a sample log. Each sample was labeled with a unique ID to reference the sample collector, sample time, source, fuel type, and other pertinent information required for the analysis. Supplemental information was added to this ID throughout sample transport and analysis to document the chain of custody. Sample chain of

custody was maintained such that trace elements, nitrogen, and sulfur results could be tracked to each sample. Chain of custody procedures were consistent with the Bulk Engine Oil Chain of Custody and Quality Documentation per API 1525A (first edition, addendum: December 2013).

The laboratory ensured that testing data met generally accepted quality assurance and quality control (QA/QC) procedures, as prescribed under Inspectorate's current ISO 9001 Certification and according to its Internal Quality Manual. After QA/QC, results of every test were sent electronically in Excel-compatible format to NESCAUM within 30 days of the sample analysis date.

Table 5. Monthly sampling schedule and number of samples collected at New York State fuel oil terminals from October 2015 to September 2016

Duplicate samples are indicated by a "d" immediately following the fuel type.

Terminal No.	Terminal Name	Oct-15	Nov-15	Dec-15	Jan-16	Feb-16	Mar-16	Apr-16	May-16	Jun-16	Jul-16	Aug-16	Sep-16
T-11-NY-1305	Global-Inwood	H	H	H	H	H	H	H	H	H	H	H	H
T-11-NY-1308	Buckeye-Brooklyn			HR	HR	HR	HR						
T-11-NY-1336	Global-Oyster Bay	H	H	H	H	H	H	H	H	H	H	H	H
T-13-NY-1352	Sprague-Bronx	H	H	H	HdR	HR	HR	HR	HR	HdR	HR	HR	HR
T-13-NY-1353	Buckeye-Bronx			Rd		R	R						
T-14-NY-1403	Global-Albany			H	H	Hd	H						
T-14-NY-1413	Global-Original	H	H	H	H	H	H	H	H	HU	HU	HU	HU
T-14-NY-1417	Sprague-Albany	H	H	HR	HR	HR	HR	H	H			HB	H
T-16-NY-1456	Buckeye-Brewerton	H	H	H	H	H	H	H	H	H	H	H	H
T-16-NY-1458	Buckeye-Buffalo	H	H	H	H	H	H	H	H	HU	Ud	HU	HU
T-16-NY-1469	Buckeye-Rochester	H	H	H	H	H	H	H	H	H	H	H	H
T-16-NY-1472	Buckeye-Rochester South			H	H	H	H						
T-16-NY-1486	Buckeye-Utica	H	H	H	H		H	H	H	H	H	H	H
T-16-NY-1488	Buckeye-Vestal	H	H	H	H	H	H	H	H	HU	Hd	HU	H
T-16-NY-1499	Global-North			H	H	H	H						
Monthly Sum													
H (No. 2 Heating Oil)		10	10	14	14	13	14	10	10	9	8	10	10
R (No. 6 Residual Oil)		-	-	3	3	4	4	1	1	1	1	1	1
U (Ultra-Low Sulfur Diesel)		-	-	-	-	-	-	-	-	3	2	3	2
B (B100 Biodiesel)		-	-	-	-	-	-	-	-	-	-	1	-
d (Duplicate Samples)				1	1	1				1	2		

3.3 Test Results

This section presents the test results of the 162 primary fuel oil samples and 6 duplicates. Also, emission factors are calculated based on the test results and compared with the previous 2010 NYSERDA study and EPA AP-42 emission factors.

3.3.1 Testing Reproducibility

As described above, Inspectorate followed procedures to test and verify the performance of its laboratory instrumentation. In addition, duplicate samples were collected to verify the collection and storage procedures. A total of 6 duplicate samples (4 heating oil, 1 ultra-low sulfur diesel, and 1 residual fuel oil) were drawn from the same sites but analyzed separately from the original samples. Table 6 shows a comparison between the trace element concentrations of the duplicate samples and the corresponding primary samples.

The paired residual fuel oil and duplicate samples had measurable concentrations in both samples for all elements. In contrast, many of the trace element concentrations in the No. 2 heating oil and No. 2 ultra-low sulfur diesel samples were below the MDL of 10 ppb (see Table 2). In all of the No. 2 oil samples used in this duplicate comparison, the trace metal concentrations of cobalt, mercury, lead, and vanadium were below the MDL of the ICP-MS analysis method. Therefore, the percent differences between the Co, Hg, Pb, and V concentrations for each duplicate and original sample could not be calculated.

Table 6. Sulfur and trace element comparison for duplicate samples

	Mn	Co	Hg	Ni	Se	Sb	Pb	V	As	Zn	N	S
No. 2 Heating Oil (4 paired samples)												
Average Percent Difference	1.61%	-	-	47.58%	7.18%	50.77%	-	-	3.85%	6.29%	5.71%	0.00%
Pairs with Measurable Conc.	1	0	0	2	2	4	0	0	2	2	1	3
No. 6 Residual Oil (1 paired sample)												
Average Percent Difference	0.44%	1.01%	1.31%	0.49%	5.81%	8.28%	3.74%	4.39%	1.49%	0.00%	0.00%	0.33%
Pairs with Measurable Conc.	1	1	1	1	1	1	1	1	1	1	1	1
No. 2 Ultra-low Sulfur Diesel (1 paired sample)												
Average Percent Difference	-	-	-	145.8%	-	191.3%	-	-	-	-	-	11.8%
Pairs with Measurable Conc.	0	0	0	1	0	1	0	0	0	0	-	1

3.3.2 Trace Element Concentrations by Fuel Type

The analytical results for trace element content in each fuel type are summarized in Table 7. Testing results from the 2010 NYSERDA study are also presented for comparison. Note that no nitrogen testing was performed for the 2010 study, therefore there are no results to compare for that element. Because only 10 ULSD samples were tested and most of the trace element concentrations in those samples were below the limit of detection, we did not estimate emission factors for this fuel type. We note that the samples of ULSD fuel collected in August 2016 showed very high mercury content (>1000 ppb), whereas all other No. 2 fuel oil samples (heating oil and ULSD) were below the mercury MDL of 10 ppb. In addition, the lone No. 2 B100 (biodiesel) sample was also collected in August 2016 and it had a reported mercury content >2000 ppb. These three samples are extreme outliers occurring during the same month at two widely separate locations, and we cannot rule out laboratory measurement error or contamination.

Table 7 shows that a significant number of No. 2 heating oil and No. 2 ultra-low sulfur diesel samples have trace element concentrations below the relevant MDL. For example, fewer than 15% of the No. 2 heating oil samples had detectable amounts (>10 ppb) of lead. Also, no heating oil samples recorded mercury levels above instrument detection limits, whereas higher concentrations were measured in No. 6 residual oil.

Table 7. Test results of trace elements in NYS fuel oil samples

Units are in ppb for all trace elements, excepting in ppm for sulfur (S) and nitrogen (N). Parentheticals in the table are the number of samples associated with the value. Elements not detected in any samples are listed as ND in the maximum row.

Current Fuel Testing Results - No. 2 Heating Oil												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	26	57	ND	181	1206	121	5239	61	525	295	11	50
Minimum	<10 (110)	<10 (80)	ND	<10 (87)	<10 (11)	<10 (99)	<10 (30)	<10 (114)	<10 (117)	<10 (72)	7	<1 (3)
Average[b]	<10	13.1	<10	12.7	246.3	<10	136.3	<10	14.0	30.1	7.9	13.3
Median	<10	<10	<10	<10	188.0	<10	45.5	<10	<10	<10	8.0	11.0
%Samples below MDL	83%	60%	100%	66%	8%	75%	23%	86%	89%	55%	0%	2%
2010 Fuel Testing Results - No. 2 Heating Oil[a]												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	ND	10	13	11	ND	114	9	144	20	66	2899	-
Minimum	<6 (102)	<1 (25)	<2 (72)	<5 (18)	<10 (27)	<5 (55)	<3 (54)	<6 (99)	<4 (85)	<6 (35)	807	-
Average[b]		2.1	2	4.3			3.2			14.8	1998	-
Median		2	<2	7			<3			17	1920	-

Current Fuel Testing Results - No. 6 Residual Oil												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	11,630	46,520	1,165	8,498	4,703	2,065	24,980	2,735	13,890	83,720	4,830	3,656
Minimum	<100 (2)	<100 (9)	<100 (10)	<100 (6)	<100 (2)	<100 (4)	7,661	455	1,470	11,000	2,860	940
Average[b]	1,970	4,792	317	1,968	1,251	1,011	13,040	1,620	6,204	56,319	3,437	2,135
Median	1,298	213	88	453	407	1,206	12,010	1,577	4,085	64,135	3,030	1,808
%Samples below MDL	10%	45%	50%	30%	10%	20%	0%	0%	0%	0%	0%	0%
2010 Fuel Testing Results - No. 6 Residual Oil[a]												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	1,650	523	ND	197	16,900	4,870	22,600	603	8,940	4,960	3,860	-
Minimum	697	<20 (8)	<25 (16)	125 (4)	3,880	1,820	11,900	<10 (2)	849	813	2,780	-
Average[b]	1,113	172		119	8,873 (6)	2,851	16,988	188	2,967	1,963	3,020	-
Median	1,145	35		125	6,930	2,755	16,650	181	2,105	1,810	2,970	-

Current Fuel Testing Results - No. 2 ULSD												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	14	ND	1493	38	1208	ND	593	36	ND	102	10	28
Minimum	<10 (5)	ND	<10 (8)	<10 (7)	<10 (2)	ND	<10 (3)	<10 (8)	ND	<10 (6)	8	<1 (1)
Average[b]	<10	<10	272.5	11.5	277.2	<10	126.8	<10	<10	36.0	8.7	14.5
Median[b]	<10	<10	<10	<10	126.0	<10	89.5	<10	<10	<10	8.0	5.0
%Samples below MDL	50%	100%	80%	70%	20%	100%	30%	80%	100%	60%	0%	20%
2010 Fuel Testing Results - No. 2 ULSD[a]												
Constituent	**Co**	**As**	**Hg**	**Se**	**Sb**	**Mn**	**Ni**	**Pb**	**V**	**Zn**	**S**	**N**
Maximum	ND	ND		5 (1)	ND	5	6	ND	ND	64	8	-
Minimum	<6 (11)	<1 (11)	<1 (1)	<5 (8)	<10 (2)	<5 (10)	<3 (8)	<4 (11)	<4 (11)	6	<3 (1)	-
Average[b]										24	5.6	-
Median										19	5	-

[a] Numbers are taken from 2010 NYSERDA fuel oil study.

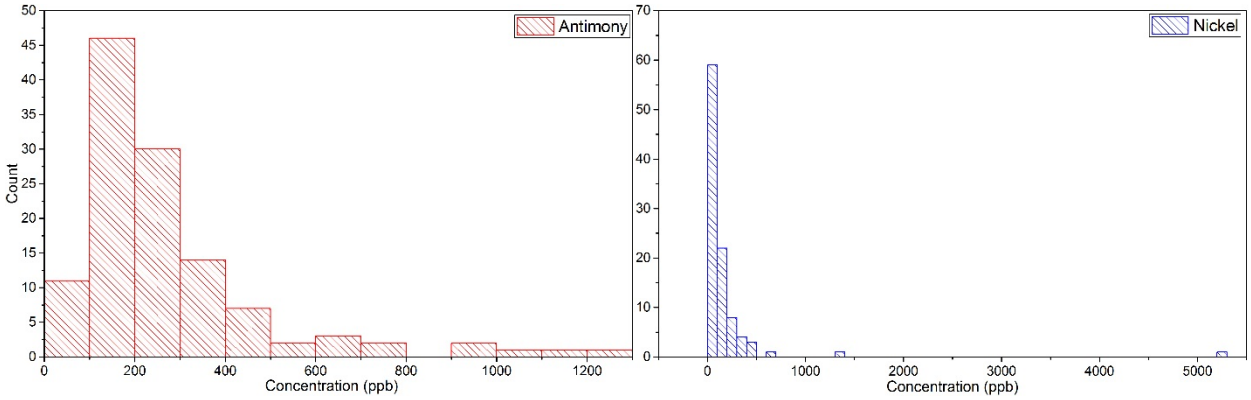
[b] Averages calculated by substituting half-MDL values for samples with levels below MDL. For No. 2 samples, averages are reported as <10 ppb for averages below MDL when substituting half-MDL values.

In comparison with the 2010 NYSERDA fuel testing results, the average, minimum, and maximum sulfur levels in No. 2 heating oil are much lower in the samples collected during 2015-2016, and consistent with the more recent sulfur limits set by NYS.

All samples of No. 2 heating oil had mercury content below the 10 ppb MDL, which is consistent with the 2010 NYSERDA study results. This is also consistent with Wilhelm et al. (2007), which reported a 1.4 to 11.3 ppb range for mercury content from 42 crude oil samples obtained in 10 states, with an average of 4.3 ppb. Similarly, a 2007 Environment Canada study found a mercury concentration range of 0.1 to 50 ppb in 109 crude oil samples collected at Canadian refineries, with an average of 2.6 ± 0.5 ppb (Hollebone and Yang 2007). Other studies (Liang et al. 1996; Bloom 2000; Rising et al. 2004) reported mercury content values at about 1 ppb or below. In contrast, earlier EPA studies (EPA 1981; 1997) estimated the concentration of mercury in No. 2 oil as <200 to 400 ppb. We note that none of these ranges approach the anomalously high mercury concentrations (>1000 ppb) reported for the two No. 2 ULSD samples collected in May 2016, which leads us to question the laboratory results.

Among all the trace elements measured in No. 2 heating oil, antimony and nickel were detected above the MDL in most of the samples. However, detected values showed some outliers based on common statistical tests. The distribution of the detected values of nickel and antimony from all samples with concentrations above the MDL is shown in Figure 10. The nickel histogram (right side of Figure 10) shows a large gap between the large majority of measured values and a few high outliers, while the gap is less for antimony (left side of Figure 10).

Figure 10. Distribution of nickel and antimony contents in No. 2 heating oil



In determining possible outliers in these results, the outlier detection method developed by Tukey (1977) is helpful because it makes no assumptions about the underlying distribution, and it does not depend on a mean or standard deviation that can be distorted by extreme outliers. Tukey's method establishes a range based on the first and third quintiles to detect outside values. The method was applied to both datasets (antimony and nickel), with six outliers identified for antimony and four outliers for nickel. Based on these results, statistics for Sb* and Ni* (i.e., outliers removed) are shown in Table 8.

Table 8. Test results for antimony (Sb*) and nickel (Ni*) in No. 2 heating oil after removing outliers

Constituent	Sb	Sb*	Ni	Ni*
# Samples above MDL	121	115	102	96
Maximum (ppb)	1206	797	5239	444
Average (ppb)	246.3	214.5	136.3	83.7
Median (ppb)	218.0	200	85.5	69

We are unable to determine if the outliers are the result of measurement error or contamination, or if they reflect actual concentrations that are much higher in a small subset of samples. In the following section, we compare these results with and without removing outliers to EPA AP-42 emission factors. Other trace elements cannot be compared in this way because of the limited number of samples above the MDL.

Sulfur content was almost the same across all No. 2 oil samples; therefore, no meaningful correlation between sulfur and other trace elements can be established. We note the Environment Canada 2007 study did not find any strong correlation between mercury and sulfur content in the crude oil samples analyzed (Hollebone and Yang 2007), nor did the earlier 2010 NYSERDA study.

Elemental analysis results of No. 6 residual oil show that sulfur, cobalt, arsenic, mercury, selenium, lead, vanadium, and zinc are higher in the more recent sample results compared to the 2010 study. On the other hand, average content of antimony, manganese, and nickel are lower. Compared to 2010 results, No. 2 ULSD analysis results show generally higher levels of trace elements where they were detectable, although a meaningful comparison is difficult due to the limited number of measurements.

None of the trace elements in No. 2 heating oil showed a distinct geographical pattern, with samples collected statewide typically showing similar concentrations. With regard to seasonal variability of trace elements in No. 2 heating oil, there appears to be a four-month window from December 2015 to March 2016 in which a higher number of samples with measured concentrations of some trace elements were recorded above the MDL of 10 ppb. During this four-month period, arsenic levels were detected above the MDL in about 90% of all No. 2 heating oil samples (50 out of 55 samples), and all terminals sampled statewide had at least two months with detectable arsenic levels in the collected samples. Measurable levels of arsenic ranged from 10 ppb to almost 60 ppb, with the majority of samples in the range of 10 to 30 ppb. For the rest of the sampling months (October to November 2015 and April to September 2016), only 2 of 77 samples had detectable arsenic levels, and both were below 20 ppb. Zinc was also detected more frequently above the MDL during the same four months, with 40 out of 55 samples having detectable zinc levels in a range from 11 ppb to 190 ppb. Selenium and manganese levels were above the MDL during the sampling months of December 2015 and January 2016, with measurable selenium in 26 out of 28 samples and measurable manganese in all 30 samples statewide. With both trace elements, measured concentrations ranged from 10 ppb to 30 ppb during these two months. As discussed above, antimony and nickel strongly spiked in June and July 2016, but our analysis indicates these two months are dominated by a subset of sample results that appear to be outliers. There is less variability across sampling months when those potential outliers are excluded. The large majority of cobalt, mercury, lead, and vanadium results were below the 10 ppb MDL across the entire 12-month sampling period; therefore, we were unable to discern any potential seasonal or spatial variability with these trace elements. We were also not able to assess seasonal or spatial differences in No. 6 residual oil trace element content due to the more limited number of samples collected. In eight of the 12 sampling months, either no or only one No. 6 oil sample was collected per month.

3.3.3 Comparison of Emission Factors

Tables 9 and 10 compare the estimated emission factors of trace elements for No. 2 heating oil and No. 6 residual oil based on this work and the 2010 NYSERDA study along with their corresponding EPA AP-42 factors. In the case of No. 2 heating oil, mercury content of all the samples was below the detection limit in this study, which is consistent with the prior 2010 NYSERDA results. Where emission factors are reported in the 2010 NYSERDA study for other trace elements (As, Se, Ni, Zn), results in this analysis indicate higher concentrations. We note, however, that more than 50% of the No. 2 heating oil samples did not have detectable levels of trace elements above the MDL, with the exceptions of Ni and Sb.

Table 9. Comparison of emission factors for No. 2 heating oil from current study, 2010 NYSERDA results, and EPA AP-42 factors

Trace Element	2010 NYSERDA		Current Work		AP-42	
	EF lb/10^6 gal	Conc. (ppb)	EF lb/10^6 gal	Conc. (ppb)	EF lb/10^6 gal	Conc. (ppb)
Co	-	-	-	<10	n/a	n/a
As	0.0147	2.1	0.091	13.1	0.56	80
Hg	0.0140	2	-	<10	0.42	60
Se	0.0301	4.3	0.089	12.7	2.08	295
Sb	-	-	1.724	246.3	n/a	n/a
Sb*	-	-	1.502	214.5	n/a	n/a
Mn	-	-	-	<10	0.83	120
Ni	0.0224	3.2	0.954	136.3	0.42	60
Ni*	-	-	0.586	83.7	0.42	60
Pb	-	-	-	<10	1.25	179
V	-	-	0.098	14.0	n/a	n/a
Zn	0.1036	14.8	0.211	30.1	0.56	80

As shown in Table 9, all emission factors computed from this analysis are lower than their corresponding EPA AP-42 emission factors, with the exception of nickel, which is about two times higher than the AP-42 emission factor. The emission factor for Ni* (i.e., outliers removed) is 1.4 times higher than its corresponding AP-42 value. The 2010 NYSERDA results for Ni, however, are 20 times lower than the AP-42 factor. For comparison to a previous fuel oil analysis, Rising et al. (2004) reported an average of 28.9 ppm Ni in No. 2 distillate oil samples collected at 13 different gas turbine installations in 10 states. The Ni in the samples ranged from 0 ppb to 185 ppb (0.2 ppb MDL). The 2010 NYSERDA results and those of this analysis are within the range reported by Rising et al. (2004), with the 2010 Ni average at the lower end of the range, and the Ni average in this study at the higher end.

For No. 6 residual oil, all emission factors except Mn and Ni were detected at higher levels compared to the 2010 NYSERDA results. The mercury emission factor is an order of magnitude higher than the 2010 emission factor, although in the current study only 10 samples of No. 6 residual oil had mercury levels above the instrumental MDL of 100 ppb. In this study, we calculate the average by using the values for those 10 samples as measured, and substituting a value of one-half the MDL (1/2 MDL = 50 ppb) for the

other 10 samples that did not have detectable levels. Studies show that substitution of nondetectable levels with one-half the MDL value is not an ideal approach to estimate a mean, but it is acceptable (Sanford et al. 1993) in a situation such as this where there are not enough data points to estimate a low-end distribution (Helsel 2009).

In comparison to EPA AP-42 emission factors for No. 6 residual oil, results for all trace elements measured in this study would indicate higher emissions rates, with some higher by greater than an order of magnitude (As, Hg, Se, Pb, Zn). We note that No. 6 residual oil had largely been phased out of use in New York City by the time of this sampling effort. The phaseout likely affected the number of samples collected during this study as No. 6 residual oil was no longer stored at the Buckeye-Brooklyn terminal during the sampling period, and we were unable to collect as many No. 6 samples as originally planned.

Table 10. Comparison of emission factors for No. 6 residual oil from current study, 2010 NYSERDA results, and EPA AP-42 factors

Trace Element	2010 NYSERDA		Current Work		AP-42	
	EF lb/10^6 gal	Conc. (ppb)	EF lb/10^6 gal	Conc. (ppb)	EF lb/10^6 gal	Conc. (ppb)
Co	8.79	1,113	15.6	1,970	6.02	762
As	1.36	172	37.9	4,792	1.32	167
Hg	0.016	2	2.51	317	0.113	14
Se	0.945	119	15.6	1,968	0.683	86
Sb	-	-	9.89	1,251	5.25	665
Mn	22.4	2,851	7.99	1,011	3	380
Ni	134	16,988	103	13,040	84.5	10,696
Pb	1.49	188	12.8	1,620	1.51	191
V	23.4	2,967	49.0	6,204	31.8	4,025
Zn	15.5	1,963	445	56,319	29.1	3,684

3.4 Summary

This report presents the results of a sampling analysis of No. 2 heating oil and No. 6 residual fuel oil samples collected at fuel oil distribution terminals across NYS from October 2015 to September 2016. These results are compared to a fuel oil sampling analysis previously reported in a 2010 NYSERDA study that covered sulfur content and the trace elements mercury (Hg), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), antimony (Sb), selenium (Se), and lead (Pb).

For No. 2 heating oil, mercury content in all of the analyzed samples was below the MDL of 10 ppb used in the current study. This result is consistent with the low mercury levels measured in the prior 2010 NYSERDA results as well as reports from other studies. Collectively, these studies consistently find lower mercury levels in No. 2 heating oil than would be estimated using the EPA AP-42 mercury emission factor for distillate oil.

Where emission factors are reported in the 2010 NYSERDA study for other trace elements (As, Se, Ni, Zn) in No. 2 heating oil, fuel oil analysis indicated higher concentrations in this more recent study. Of particular note, nickel levels in No. 2 heating oil were higher than the 2010 NYSERDA results by greater than an order of magnitude, but both sets of study results were within the range of nickel levels measured in No. 2 distillate oil samples collected in 10 states as reported in an earlier study (Rising et al. 2004).

For No. 6 residual oil, all elements in the analysis except antimony, manganese, and nickel were detected at higher levels compared to the 2010 NYSERDA results. The mercury emission factor was an order of magnitude higher than the 2010 emission factor. In this more recent study, however, only 10 samples of No. 6 residual oil had mercury levels above the instrumental MDL, and the average was calculated by substituting half-MDL values for the other 10 samples without measurable concentrations.

In comparison to EPA AP-42 emission factors for No. 6 residual oil, all trace elements measured in this study suggested higher emission factors, with some higher by greater than an order of magnitude (As, Hg, Se, Pb, Zn). We note that No. 6 residual oil was largely phased out of use in New York City by the time of this sampling program.

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